

## MOLECULAR MECHANISMS OF SCALE DEPOSITION

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Scales do not develop equally on different substrates, even when bulk physicochemical conditions are the same. The reasons for these differential developments, one must presume, are due to subtle features of the near-surface region, either composition or structure. We intend to focus our studies on the structural aspects, including concerns about the molecular structures of solvated components that may be involved with the surface reactions.

This approach is richly mechanistic in outlook. It involves concepts of stereo constraints on the chemical processes by which solutes exchange atoms or electrons with substrates. These constraints are a consequence of the more or less regular pattern of electropotential that exists at a crystalline surface. In principle, the electropotential pattern can be manipulated either through the substrate (more precisely by selecting or designing substrates that have desirable patterns) or through the components in the near-surface liquid which modify the basic substrate-induced patterns there.

### Discussion

At the Idaho National Engineering Laboratory, we are embarking into basic studies about how minerals develop from aqueous solutions. Our first studies will involve the buildup of scale in a geothermal context. The project has just begun, hence no solid results are available now for reporting. The purpose of saying anything at all at this time is to outline the emphasis we plan to give to the topic, which contrasts to the approaches commonly used.

An important premise of our approach considers the space in which heterogeneous reactions take place, namely, the boundary layer. The interesting molecular processes occur within this boundary layer and presumably are affected by its structure. The boundary layer structure depends upon the substrate structure, solution composition, and physical conditions. Features of the solutes are believed to be better (or poorer) adapted to meeting the structural requirements of the boundary layer reactions. These structural requirements and relationships are part of the information we seek. It is through these that we hope to find explanations for particular details of scale morphology and development.

The kinds of details we find interesting are shown in Figures 1, 2, and 3.

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These figures concern an experiment in which geothermal water from Raft River No. 1 was flowed for 3 weeks through a cooled tube of 1/8-inch O.D. carbon steel tubing.\* The figures are of transverse sections of the tubing and show the scale-tube interface. Magnifications are 2000 x, hence curvature of the section is not obvious.

The figures are electron microprobe data that have been cast into isopleths. Both Si and Fe are shown on each map--Fe by the heavy lines. The busy detail in the corner areas represents the carbon steel which serves as an Fe standard. Fe isopleths refer to photon returns from electron-stimulated Fe atoms and are approximately related to Fe content of the scale. Spacing of the isopleths corresponds to 10 percent increments of the maximum photon return detected in the scan area. These isopleths may be read just like a topographic map. The space involved with the Fe isopleths that are sub-parallel corresponds to the rust layer on the inside of the tube. The extra-heavy Fe isopleth concerns classical compositions of Fe-bearing oxides and hydroxides. When adjustment is made for the lesser absorption of Fe photons by oxygen, all compositions between goethite and magnetite give similar photon returns, namely 68 to 71 percent of the return expected from pure Fe. Thus, most of the space occupied by the "rust" involved non-classical compositions or mixtures of Si and Fe phases.

Si data is indicated by shading between isopleths, superimposed on the Fe maps. Shading is done in alternate bands, 10-20, 30-40, 50-60, 70-80, where the numbers represent percents of maximum photon return within the scan area. There was no Si standard in the probe setup, so we have no way of knowing what Si content the maximum Si photon return refers to. The shading thus shows lateral extent of Si deposition with a hint about density of the deposit. Large numbers on the figures refer to the location of the specimen in feet downflow from the hot end of the tube.

In Fig. 1, local maxima of Si depositions correspond in space to local excesses of Fe. Also, a definite, though low-level, deposition of Si exists remote from the Si maxima.

In Fig. 2, the embayment of Fe contours suggests pit corrosion which is reflected in the Si contours by a displaced site of local excess of deposition.

In Fig. 3, the local excess of Fe without a Si cover looks like an artifact, perhaps a consequence of the time interval between shutdown of the experi-

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\*Input was directly from the well head. Pressures were 150 to 170 psi, temperature input was 125 to 130C, cooled to 30C during a residence time near 12 seconds. Water composition involves about 1300 ppm total dissolved solids, of which 80 percent is NaCl. SiO<sub>2</sub> content is 100 to 130 ppm.

ment and cut-up of the tube for making metallographic mounts. The ends of the tube were crimped to deny  $O_2$  (air) access to the inside; perhaps crimping was not fully successful.

The fourth figure comes from some work I did several years ago when studying the conversion of  $CaCO_3$  (calcite) to  $PbCO_3$  (cerussite). The reason for showing the diagram is one of analogy. We have a substrate ( $CaCO_3$ ) which serves both as a support for the scale ( $PbCO_3$ ) and a source of one of the scale components.

Figure 4 represents several distinctive events that are involved with the reaction, viz.

1. adsorption of  $Pb(II)$  on the calcite surface
2. arrangement of  $Pb(II)$  and  $CO_3$  on the calcite surface to nucleate a cerussite crystal
3. adsorption of  $Pb(II)$  on cerussite
4. arrangement of  $Pb(II)$  on the cerussite surface to add to the crystal structure
5. arrangement of  $CO_3$  on the cerussite surface to add to the crystal structure
6. nucleation of etch pits on the calcite
7. movement of steps on the calcite surface
8. migration of  $CO_3$  away from etch pits in the calcite

In addition, ions and molecules that are nonessential to the scale composition are sorbed on its surfaces where they affect the events listed above. These nonessential sorbates may control crystal habit of the scale phase and in combination it seems plausible that they might be chosen to totally interfere.

One commonly does research in a system like this in order to identify which of the events determines the overall reaction rate, but the question of rate control may be fundamentally ambiguous. In the closed system calcite  $Pb(II)$  solution the reaction was observed to pass through several stages when monitored in terms of the rate of consumptions of  $Pb(II)$ . Each stage was limited in overall rate according to the following sequence:

Stage 1: nucleation rate of new cerussite crystals,

Stage 2: surface area of cerussite: Consumption of lead by nucleation of new crystals becomes small compared to the consumption by crystal growth,

Stage 3: production and transport of  $\text{CO}_3$  to sites of precipitation on the cerussite,

Stage 4: diffusion of  $\text{Pb(II)}$  to the sites of precipitation.

Stage 4 occurs last, as the  $\text{Pb(II)}$  concentration approaches zero.

In principle, the scaling reactions are vulnerable to interference at each event in the deposition process. Eventually, we may devise techniques, based on detailed knowledge of molecular processes, which inhibit or promote scale deposition in places as we choose.

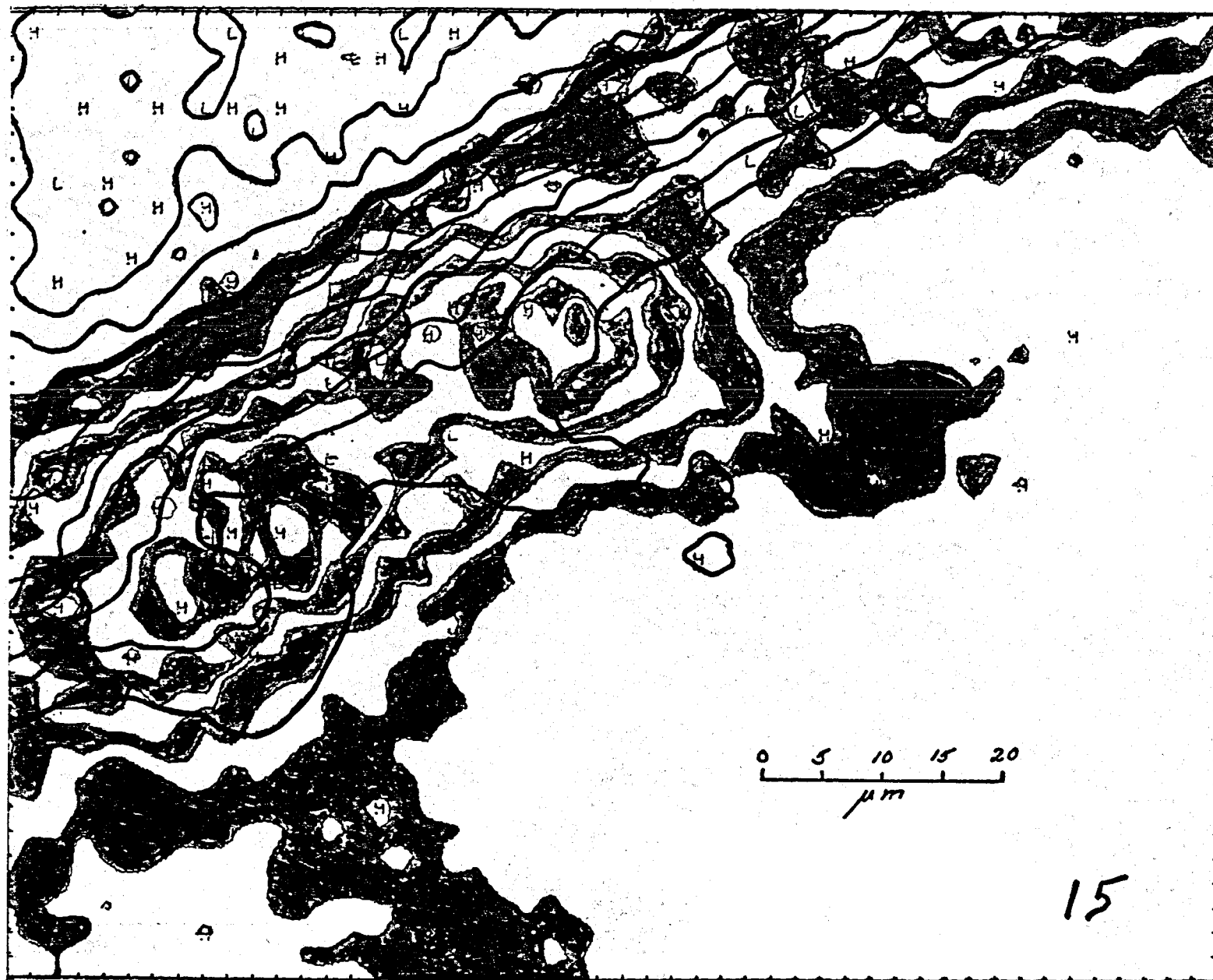


FIGURE 1: Fe AND Si SCALE ON CARBON STEEL

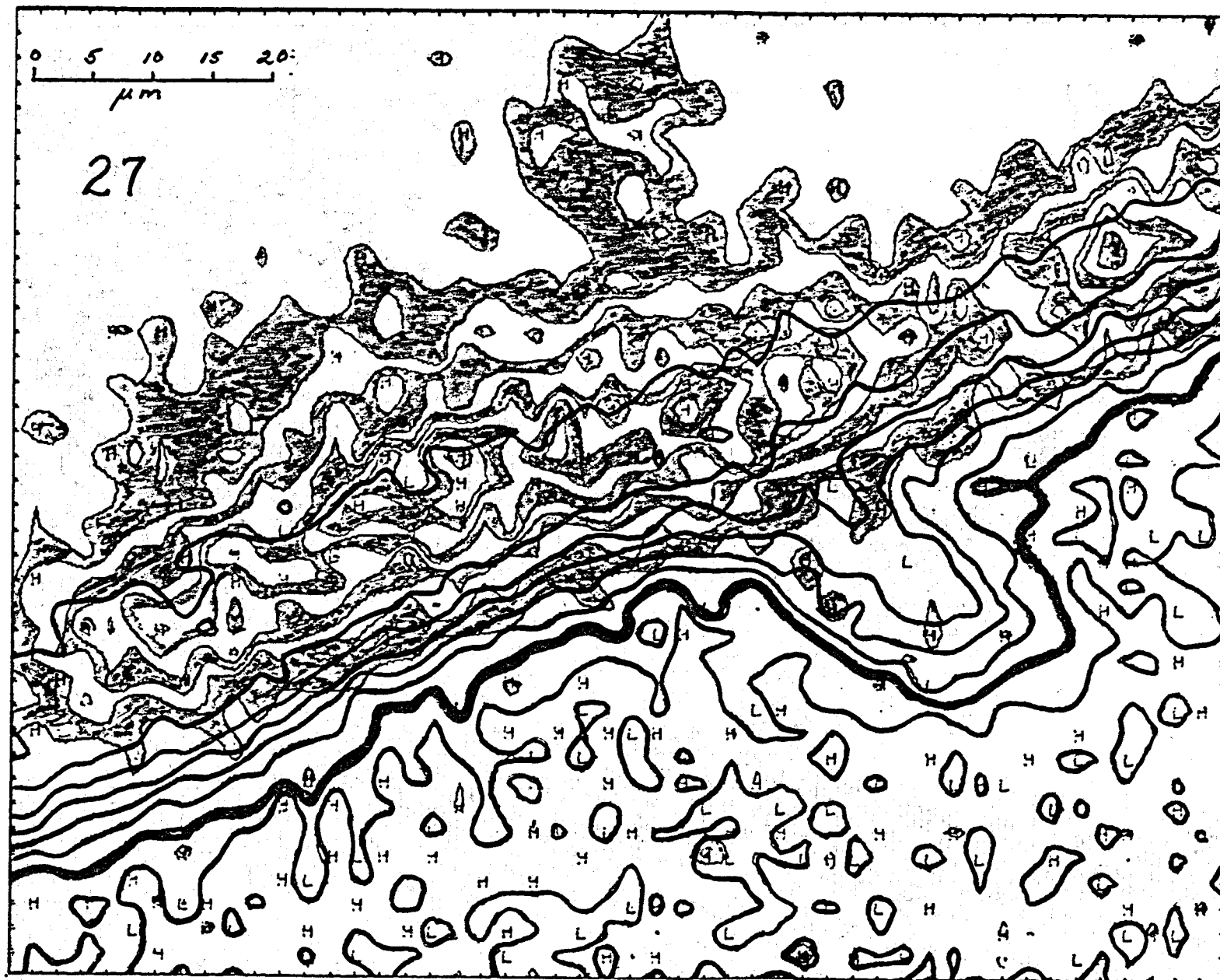


FIGURE 2: Fe AND SI SCALE ON CARBON STEEL



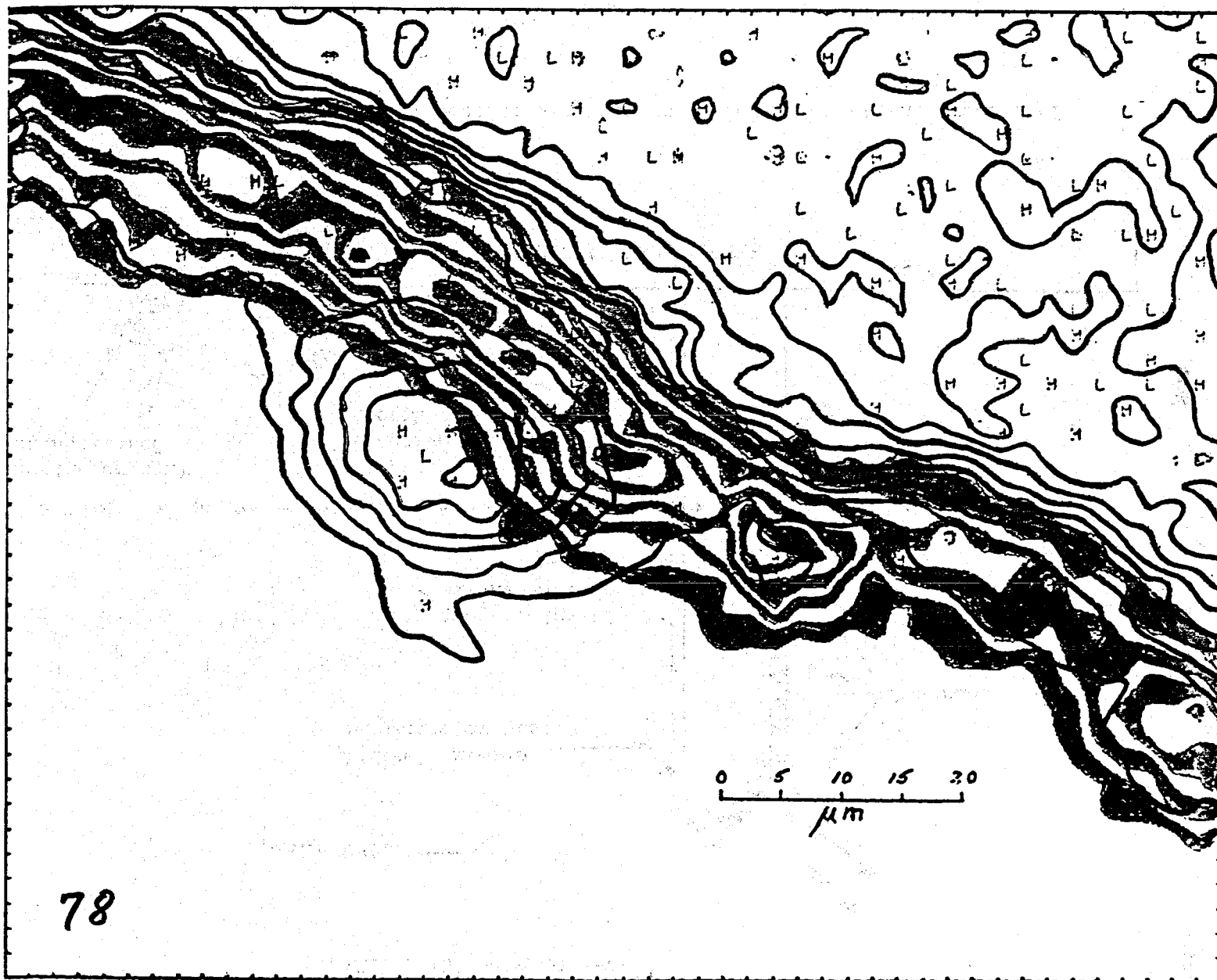


FIGURE 3: FE AND SI SCALE ON CARBON STEEL

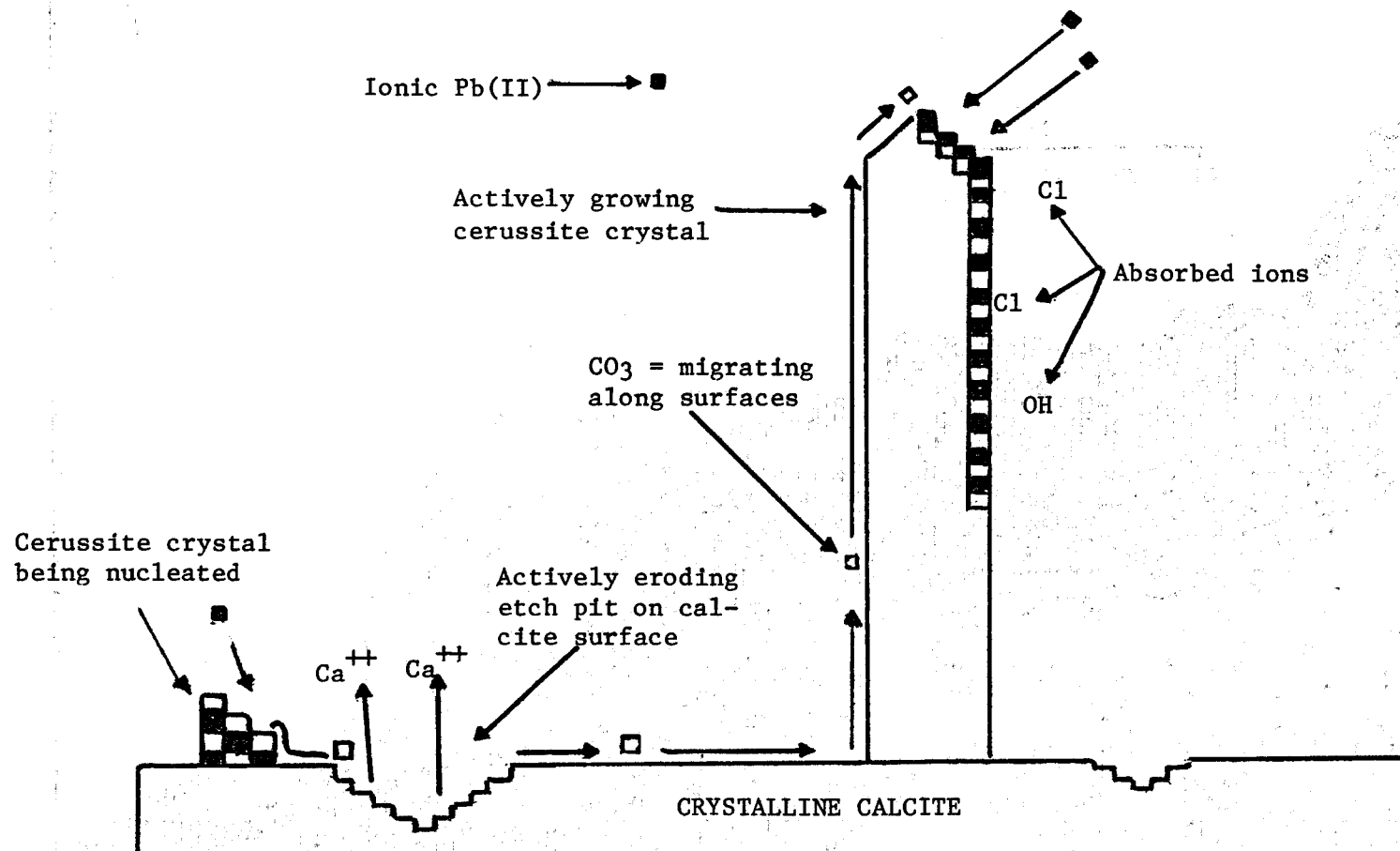
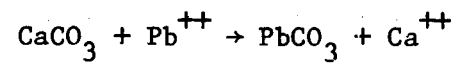


Fig. 4. Schematic representation of cerussite formation at the expense of calcite.